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(19)(CA) # CANADIAN PATENT

(54) BLEACHING COMPOSITIONS

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The invention here presented is broadly in the field of bleaching; more particularly it relates to activators for oxygen-releasing compounds and relates especially to activators formed from peracid precursors.

The use of per-compounds which liberate hydrogen peroxide such as inorganic perhydrates, which, when dissolved liberate hydrogen peroxide enclosed in their crystal lattice (e.g., perborates, perphosphates, persilicates) and peroxides which yield hydrogen peroxide by hydrolysis (e.g., sodium peroxide or certain percarbonates) in domestic or industrial laundering is well known. There are, in particular, detergent compositions in which per-compounds such as sodium perborate frequently comprises between 1% and 35% of the total composition.

Hydrogen peroxide and the precursors which liberate it in solution are good oxidizing agents for removing certain stains from cloth, especially stains caused by wine, tea, coffee, cocoa, fruits, etc. However, hydrogen peroxide and its precursors have been found to bleach quickly and most effectively only at a relatively high temperature, e.g., about 80°C to 100°C. Since it is often impracticable or inconvenient to boil the wash water the full potential of oxygen bleaches has not yet been realized because of their poor bleaching at temperatures below 80°C. Since these bleaches are relatively safe both in concentrated form and on colors, and since they can be formulated directly in the detergent, it is desirable to provide a process for bleaching with per-oxygen compounds and compositions containing them, which provide effective

bleaching and stain removing properties at temperatures below boiling, e.g., 25° - 80°C.

Most bleaching is done in an alkaline medium. It is believed, without being limited to any theory, that hydrogen peroxide ionizes in an alkaline medium into a hydrogen ion and a negatively charged perhydroxyl ion. The perhydroxyl ion can react with additional hydrogen peroxide to yield active oxygen which is also negatively charged. Both the perhydroxyl ion and the active oxygen ion can bleach by oxidizing a substrate via election transfer. Since materials to be bleached are usually negatively charged, the material and the perhydroxyl ion or active oxygen mutually repel each other and it takes high temperatures before the perhydroxyl ion or active oxygen has sufficient energy to overcome this repulsion. An activator which has a higher oxidation potential than the per-compound alone would result in improved bleaching at lower temperatures.

It is known that peracids which are formed from hydrogen peroxide and an acid are stronger oxidizing agents than hydrogen peroxide itself. However, peracids are relatively unstable and cannot be used as such but only formed in-situ from a peroxygen compound such as sodium perborate and a suitable peracid precursor.

The present invention relates to a process and composition for forming peracids in-situ in order to obtain significant bleaching effects at temperatures of about 25° - 80°C., preferably about 50° - 70°C. Broadly then, the invention relates to the process for bleaching materials at

temperatures below boiling, e.g., about 25° - 80°C., in aqueous solution which comprises reacting a per-compound of the oxygen-releasing type, an acyl-alkyl ester wherein the acyl group has 2 to 8 carbon atoms and an ester-hydrolyzing enzyme which in aqueous media liberates said acyl moiety from said ester.

Thus this invention provides a process for bleaching materials at a temperature of at least 25°C. in which a fabric or textile material to be bleached is contacted with an aqueous washing solution containing an effective amount of an oxygen-releasing per-compound, characterized by the step of incorporating an acyl-alkyl ester and an ester hydrolyzing enzyme into said washing solution. It also relates to a bleaching composition containing an oxygen-releasing per-compound, characterized in that it also contains an acyl-alkyl ester having the general formula $R_1C(=O)-OR_2$ wherein the acyl group $R_1C(=O)$ contains 2 to 8 carbon atoms, and R_2 is an alkyl group of 1 to 10 carbon atoms, and an ester-hydrolyzing enzyme composition which hydrolyzes said acyl-alkyl ester, wherein said composition is effective for bleaching materials at a temperature of at least 25°C.

In the present invention, the ester and ester-hydrolyzing enzyme are precursors in the formation of per-acids in situ, i.e., in bleaching solution. The reactive carboxylic group formed reacts with the per-compounds to form per-acids which have the requisite bleaching effects at temperatures of about 25° - 80°C.

Per-compounds which are oxygen-releasing and employable in the present invention are hydrogen peroxide, alkali metal peroxides such as sodium perborate and potassium perborate, alkali metal perphosphates such as sodium perphosphate and potassium perphosphate, alkali metal persilicates, such as sodium persilicate and potassium persilicate, and alkali metal percarbonates such as sodium percarbonate and potassium percarbonate.

The per-compounds are generally present in the ratio by weight of per-compound to ester-substrate of about 1.0 to 6.0 to about 6.0 to 1.0; the preferred ratios being

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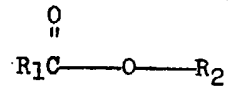
about 1/2 to 3 to about 2 to 1. The per-compounds are typically present in bleaching compositions in amount of about 1.0 to about 40% by weight, preferably 3 to 20% and more preferably 5 to 15% by weight of the total composition.

Generally, the esters employable in the present invention are acyl-alkyl esters having the general formula:



wherein R_1 is part of the organic moiety making up the acyl portion of the ester and has 1 to 8 carbon atoms in its chain and R_2 is the alkyl moiety of the ester and has 1 to 8 carbon atoms in its chain. Examples of preferred acyl-alkyl esters are esters of acetic acid such as methyl acetate, ethyl-acetate, propyl acetate, isopropyl acetate and acetals having the formula $CH_3CH<^{OR_1}_{OR_2}$ wherein R_1 and R_2 are radicals having 2 to 8 carbon atoms in their chain, and other aliphatic esters such as methyl-butyrate, ethyl butyrate, propyl butyrate, and isopropyl butyrate.

The amount by weight of ester employable in the bleaching process and composition is dependent upon the amount of per-compound present.

The ester hydrolyzing enzymes are usually specific for the simple aliphatic esters employable in this invention. Generally, the ester hydrolyzing enzymes this invention makes use of are esterases and lipases. Examples of preferred esterases are acetylesterase and carboxylesterase. These esterases hydrolyze carboxylic esters and have wide distribution in mammalian tissues, insects, plants, citrus fruits and

fungi. A preferred preparation is from horse liver [Connors, W.M., Pihl, A., Dounce, A.L. & Stotz, E. (1950), J. biol. Chem. 184, 29; Burch, 1954], with a specific activity of 0.25 m-mole of ethyl butyrate/mg. protein N/min.

Examples of preferred lipases are plant lipases, pancreatic lipase and gastric lipase. These lipases also hydrolyze carboxylic esters and are present in mammalian pancreas and oats. A preferred preparation is from pig pancreas [Sarda, L., Marchis-Mouren, G., Constantin, M.J. & Desnuell, P. (1957), Biochim. biophys. Acta, 23, 264], with a specific activity of 63 m-moles of olive oil/mg. protein N/min.

The amount of enzyme employed depends upon the amount of ester-substrate present. The ratio of ester to enzyme is about 30 to 1 to about 5 to 1 and preferably about 20 to 1 to about 10 to 1. The amounts of enzyme required also varies with the specific activity of the enzyme employed. With regard to the recited ratio, it is assumed that the specific activity of the enzyme employed is of the order of magnitude set out above.

The invention also relates to the instant bleaching processes carried out in the presence of and bleaching compositions containing organic detergent selected from the group consisting of water-soluble soap, and synthetic organic detergents.

Examples of suitable water-soluble soaps include the water-soluble salts, e.g., the sodium, ammonium, and alkylolammonium salts, of higher fatty acids or resin salts containing about 8 to 20 carbon atoms, preferably 10 to 18

carbon atoms. Suitable fatty acids can be obtained from oils and waxes of animal or vegetable origin, e.g., tallow, grease, coconut oil, tall oil and mixtures thereof. Particularly useful are the sodium and potassium salts of the fatty acid mixtures derived from coconut oil and tallow, e.g., sodium coconut soap and potassium tallow soap.

Synthetic organic detergents employable in the present invention comprise detergents selected from the group consisting of anionic, nonionic, amphoteric, polar nonionic and cationic detergents.

Examples of suitable anionic detergents which fall within the scope of the anionic detergent class include the water-soluble salts, e.g., the sodium, ammonium, and alkylol-ammonium salts, of higher fatty acids or resin salts containing about 8 to 20 carbon atoms, preferably 10 to 18 carbon atoms.

The anionic class of detergents also includes the water-soluble sulfated and sulfonated synthetic detergents having an alkyl radical of 8 to 26, and preferably about 12 to 22 carbon atoms, in their molecular structure. (The term alkyl includes the alkyl portion of the higher acyl radicals.)

The usual non-ionic surfactants can be used, such as condensation products of alkyl phenols or alkylthiophenols with ethylene oxide or other ethylene oxide condensation products with higher fatty alcohols, monoesters of hexahydric alcohols, etc.

The amphoteric detergents which can be used in the compositions of this invention are generally water-soluble

salts of derivatives of aliphatic amines which contain at least one cationic group, e.g. non-quaternary nitrogen, quaternary ammonium, or quaternary phosphonium group, at least one alkyl group of about 8 to 18 carbon atoms and an anionic water-solubilizing carboxyl, sulfo, sulfato, phosphato or phosphono group in their molecular structure. The alkyl group may be straight chain or branched and the specific cationic atom may be part of a heterocyclic ring.

The polar nonionic detergents of this invention include open-chain aliphatic amine oxides of the general formula $R_1R_2R_3N\rightarrow O$. For the purposes of this invention, R_1 is an alkyl, alkenyl, or monohydroxyalkyl radical having about 10 to 16 carbon atoms. R_2 and R_3 are each selected from the group consisting of methyl, ethyl, propyl, ethanol, and propanol radicals.

The usual cationic detergents can be used such as the diamines of the general formula $RNHC_2H_4NH_2$, whereby R is an alkyl group of about 12 to 22 carbon atoms, or compounds having the general formula $R'CONHC_2H_4NH_2$ is an alkyl group of about 12 to 18 carbon atoms, further quaternary ammonium compounds, anionic or non-ionic surfactants are preferred, namely salts of higher alkyl benzene sulfonates, higher alkyl sulfonates and higher fatty acid monoglyceride sulfate.

The concentration of the organic detergents such as water-soluble soaps and synthetic organic detergents in the inventive compositions will generally range from 4 to 40% and preferably 15 to 35% by weight.

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The compositions can also contain conventional ingredients such as builder salts. Suitable representatives include the following: Trisodium phosphate, tetrasodium pyrophosphate, sodium acid pyrophosphate, sodium tripolyphosphate, sodium monobasic phosphate, sodium dibasic phosphate, sodium hexamethaphosphate, sodium metasilicate, sodium silicate (Na_2O/SiO_2 of 1/1.6 to 1/3.2), sodium carbonate, sodium sulfate, borax, ethylene diamine tetraacetic acid tetrasodium salts, trisodium nitrilotriacetate, citrates, e.g., sodium citrate, citric acid, glycollates, e.g., sodium glycollate, phosphonates, diphosphonates, organic polyelectrolytes, e.g., vinyl methyl ethermaleic anhydride interpolymers and water-soluble salts thereof (alkali metal, ammonium, amine, etc.); polymaleic anhydride and water-soluble salts (sodium, potassium, ammonium, etc.) and mixtures thereof.

Usually substantial amounts of compatible "builder" materials will be present in the invential compositions, the amounts being in order of about 40 to 90% by weight, preferably about 65 to 85% by weight of the composition. The compositions may also contain other conventional ingredients, for example, antirediposition agents such as sodium carboxymethyl cellulose; suds builders such as ammonia amides N-alkyl amides, and alkanolamides of fatty acids (e.g., coconut monethanolamide and lauroyl and myristoyl glycerol amides, ethanol amides and isopropanol amides); optical bleaching agents; color; and perfume.

The following examples further illustrate this invention:

EXAMPLE I

	Percent by Weight
Sodium linear tridecyl benzene sulfonate	35.0
Anhydrous pentasodium tripolyphosphate	40.0
Sodium perborate	8.0
Ethylbutyrate	8.0
Acetylesterase	0.8
Perfume	0.5
Moisture and Additives such as brighteners, color, etc.	7.7
	100.0

EXAMPLE II

Sodium tetrapropylbenzene sulfonate	12.0
Sodium carbonate	35.0
Potassium persilicate	30.0
Propyl acetate	10.0
Carboxylesterase	0.5
Perfume	0.5
Moisture and Additives such as brighteners, color, etc.	2.0
	100.0

EXAMPLE III

Sodium dodecylbenzene sulfonate	18.0
Sodium tripolyphosphate	35.0
Monoethanolamide of coconut oil fatty acid	2.5
Sodium silicate	7.0
Sodium sulfate	9.0
Magnesium silicate	1.0
Sodium perborate	5.0
Ethyl acetate	10.0

EXAMPLE III cont.

	Percent by Weight
Pancreatic lipase	0.5
Perfume	1.0
Moisture and Additives such as brighteners, color, etc.	11.0
	100.0

A washing solution is prepared by dissolving 12.5 grams or 5 grams per liter of any of the compositions recited in Examples I-III in tap water having a hardness of 50 ppm. Soiled household laundry is immersed in the washing solution for 10 minutes at about 50°C. and stirred after which the laundry is removed, rinsed in water and dried. The bleaching effects are observed. Broadly, the improved process for bleaching comprises contacting the fabric or textile material to be bleached with an aqueous washing solution containing effective amounts of an oxygen-releasing per-compound, an acyl-alkyl ester and an ester hydrolyzing enzyme at temperatures ranging from about 25° to 80°C. from 1 up to about 30 minutes and preferably at about 50°C. for 5 to 15 minutes. The material to be treated may be pre-soaked or allowed to stand in the aqueous washing solution or the solution containing the material may be stirred or agitated.

It is to be understood that the invention is not limited to the specific embodiments described above. Various modifications can be made in the process and in the compositions without departing from the spirit or scope of the invention.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for bleaching materials at a temperature of at least 25°C. in which a fabric or textile material to be bleached is contacted with an aqueous washing solution containing an effective amount of an oxygen-releasing per-compound, characterized by the step of incorporating an acyl-alkyl ester and an ester-hydrolyzing enzyme into said washing solution.

2. A process according to claim 1, characterized in that the ratio of said per-compound to said ester is about 1 to 6 to about 6 to 1 and the ratio of said ester to said enzyme is about 30 to 1 to about 5 to 1.

3. A process according to claim 1, wherein said per-compound is present in an amount of about 1% to about 40% by weight of the total composition.

4. A process according to claim 1, wherein the aqueous solution also contains a detergent selected from the group consisting of soap, synthetic organic detergent and mixtures thereof.

5. A process according to claim 4, wherein said organic detergent is present in an amount of about 4% to 40% by weight of the total composition.

6. A process according to any one of claims 1 to 3, wherein said per-compound is selected from the group consisting of hydrogen peroxide, alkali metal peroxides, perborates, perphosphates, persilicates, and per-carbonates.

7. A process according to any one of claims 1 to 3, characterized in that said acyl-alkyl ester has the general formula $R_1C(=O)-OR_2$ wherein R_1 and R_2 have 1 to 10 carbon atoms in their chain.

8. A process according to any one of claims 1 to 3, characterized in that said ester-hydrolyzing enzyme is selected from the group consisting of esterases and lipases.

9. A bleaching composition containing an oxygen-releasing per-compound, characterized in that it also contains an acyl-alkyl ester having the general formula $R_1C(=O)-OR_2$ wherein the acyl group $R_1C(=O)$ contains 2 to 8 carbon atoms, and R_2 is an alkyl group of 1 to 10 carbon atoms, and an ester-hydrolyzing enzyme composition which hydrolyzes said acyl-alkyl ester, wherein said composition is effective for bleaching materials at a temperature of at least 25°C.

10. A bleaching composition according to claim 9, wherein said per-compound is selected from the group consisting of hydrogen peroxide, alkali metal (e.g. sodium and potassium) peroxides, perborates, perphosphates, persilicates, and percarbonates.

11. A bleaching composition according to claim 9, wherein said ester-hydrolyzing enzyme is selectedfrom the group consisting of esterases and lipases.

12. A bleaching composition according to claim 11, wherein said esterase is selected from the group consisting of acetylesterase and carboxyl-esterase and said lipase is selected from the group consisting of plant lipases, pancreatic lipase and gastric lipase.

13. A bleaching composition according to any one of claims 9 to 11, wherein the ratio of said per-compound to said ester is about 1 to 6 to about 6 to 1 and the ratio of said ester to said enzyme is about 30 to 1 to about 5 to 1.

14. A bleaching composition according to any one of claims 9 to 11, wherein said per-compound is present in an amount of about 1% to about 40% by weight of the total composition.

15. A bleaching composition according to claim 9, wherein also present is an organic detergent selected from the group consisting of soap, organic synthetic detergent and mixtures thereof.

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16. A bleaching composition according to claim 15, wherein said organic detergent is present in an amount of about 4% to 40% by weight of the total composition.